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(54) **Title:** PERFLUOROPOLYETHERS AND PROCESSES THEREFOR AND THEREWITH

(57) **Abstract:** A perfluoropolyether, a composition comprising the perfluoropolyether, a process for producing the perfluoropolyether, and a process for improving the thermostability of grease or lubricant are provided. The perfluoropolyether comprises (1) perfluoroalkyl radical end groups in which the radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl end groups or (2) at least one bromine or iodine atom at the primary position of the perfluoropolyether.

PERFLUOROPOLYETHERS AND PROCESSES THEREFOR AND THEREWITH

FIELD OF THE INVENTION

The invention relates to a perfluoropolyether having improved thermostability over the presently available perfluoropolyethers, to a process therefor, and to a process therewith.

BACKGROUND OF THE INVENTION

Hereinafter trademarks or trade names are shown in upper case characters.

Perfluoropolyethers (hereinafter PFPE) are fluids having important uses in oils and greases for use under extreme conditions. A property shared by the class is extreme temperature stability in the presence of oxygen and they find use in tribological or lubrication applications. Among their advantages as extreme lubricants is the absence of gums and tars among the thermal decomposition products. In contrast to the gum and tar thermal degradation products of hydrocarbons, the degradation products of PFPE fluids are volatile. In actual use, the upper temperature limit is determined by the stability of the oil or grease. Lewis acids, metal fluorides such as aluminum trifluoride or iron trifluoride, are formed as a result of heat at microscale loci of metal to metal friction; for instance as stationary bearings are started in motion. Thus the PFPE stability in the presence of the metal fluoride, although lower than the stability in the absence of the metal fluoride, establishes the upper performance temperature. The three commercial PFPEs, KRYTOX (from E.I. du Pont de Nemours and Company, Inc., Wilmington DE), FOMBLIN and GALDEN (from Ausimont/Montedison, Milan, Italy) and DEMNUM (from Daikin Industries, Osaka, Japan) differ in chemical structure. A review of KRYTOX is found in *Synthetic Lubricants and High-Performance Fluids*, Rudnick and Shubkin, Eds., Marcel Dekker, New York, NY, 1999 (Chapter 8, pp. 215 – 237). A review of FOMBLIN and GALDEN is found in *Organofluorine Chemistry*, Banks et al., Eds., Plenum, New York, NY, 1994, Chapter 20, pp. 431 - 461, and for DEMNUM, in *Organofluorine Chemistry*, Chapter 21, pp. 463 – 467.

The anionic polymerization of hexafluoropropylene epoxide as described by Moore in US Patent 3,332,826 can be used to produce the KRYTOX fluids. The resulting poly(hexafluoropropylene epoxide) PFPE fluids are hereinafter described as poly(HFPO) fluids. The initial polymer has a terminal acid fluoride, which is hydrolyzed to the acid followed by fluorination. The structure of a poly(HFPO) fluid is shown by Formula 1:

$$CF_3\text{-}(CF_2)_2\text{-}O\text{-}[CF(CF_3)\text{-}CF_2\text{-}O]_s\text{-}R_f \qquad \text{(Formula 1)}$$

where s is 2 - 100 and R_f is a mixture of CF_2CF_3 and $CF(CF_3)_2$, with the ratio of ethyl to isopropyl terminal group ranging between 20:1 to 50:1.

DEMNUM fluids are produced by sequential oligomerization and fluorination of 2,2,3,3-tetrafluorooxetane (tetrafluorooxetane), yielding the structure of Formula 2.

$$F\text{-}[(CF_2)_3\text{-}O]_t\text{-}R_f^2 \qquad \text{(Formula 2)}$$

where R_f^2 is a mixture of CF_3 or C_2F_5 and t is 2 - 200.

A common characteristic of the PFPE fluids is the presence of perfluoroalkyl terminal groups.

The mechanism of thermal degradation in the presence of a Lewis acid such as aluminum trifluoride has been studied. Kasai (Macromolecules, Vol. 25, 6791-6799, 1992) discloses an intramolecular disproportionation mechanism for the decomposition of PFPE containing $\text{-}O\text{-}CF_2\text{-}O\text{-}$ linkages in the presence of Lewis acids.

FOMBLIN and GALDEN fluids are produced by perfluoroolefin photooxidation. The initial product contains peroxide linkages and reactive terminal groups such as fluoroformate and acid fluoride. These linkages and end groups are removed by ultraviolet photolysis and terminal group fluorination, to yield the neutral PFPE compositions FOMBLIN Y and FOMBLIN Z represented by Formulae 3 and 4, respectively

$$CF_3O(CF_2CF(CF_3)\text{-}O\text{-})_m(CF_2\text{-}O\text{-})_n\text{-}R_f^3 \qquad \text{(Formula 3)}$$

where R_f^3 is a mixture of $\text{-}CF_3$, $\text{-}C_2F_5$, and $\text{-}C_3F_7$; (m + n) is 8 - 45; and m/n is 20 - 1000; and

$$CF_3O(CF_2CF_2\text{-}O\text{-})_p(CF_2\text{-}O)_qCF_3 \qquad \text{(Formula 4)}$$

where (p + q) is 40 - 180 and p/q is 0.5 - 2. It is readily seen that Formulae 3 and 4 both contain the destabilizing -O-CF_2-O- linkage since neither n nor q can be zero. With this -O-CF_2-O- linkage in the chain, degradation within the chain can occur, resulting in chain fragmentation.

For PFPE molecules with repeating pendant -CF_3 groups, Kasai discloses the pendant group provides a stabilizing effect on the chain itself and for the alkoxy end groups adjacent to a -CF(CF_3)-. Absent the -O-CF_2-O- linkage, the PFPE is more thermally stable, but its eventual decomposition was postulated to occur at end away from the stabilizing -CF(CF_3)- group, effectively unzipping the polymer chain one ether unit at a time.

Therefore, there is substantial interest and need in increasing the thermal stability of PFPE fluids.

Perfluoropolyether primary bromides and iodides are a family of highly useful and reactive chemicals that can be used, for example, as lubricants, surfactants, and additives for lubricants and surfactants. See, e.g., Journal of Fluorine Chemistry **1990**, *47*, 163; **1993**, *65*, 59; **1997**, *83*, 117; **1999**, *93*, 1; and **2001**, *108*, 147; Journal of Organic Chemistry **1967**, 32, 833. *See also*, US Patents 3,332,826; 3,505,411; 4,973,762; 5,278,340; 5,288,376; 5,453,549; and 5,777,174.

Useful mono-functional (Formula A) and di-functional (Formula B) acid fluorides, which can be used in the present invention can be prepared cab be prepared as follows.

Φ-CF(CF_3)CF_2OCF(CF_3)C(O)-F Formula A

FC(O)CF(CF_3)OCF_2CF(CF_3)-Φ'-CF(CF_3)CF_2OCF(CF_3)C(O)F Formula B

where Φ and Φ' are respectively monovalent and divalent perfluoropolyether moieties. Additionally other acid fluorides of Formulae I and II are the reaction products formed from the polymerization of hexafluoropropylene oxide alone or with suitable starting materials, 2,2,3,3-tetrafluorooxetane, or the photooxidation of hexafluoropropylene or tetrafluoroethylene.

Secondary iodides from the acid fluorides can be prepared, for example at 0 - 60 °C using radiation from a photochemical lamp, for instance a lamp with an

ultra-violet light output in the wavelength range of 220 - 280 nm (US Patent 5,288,376).

The usefulness of this invention is demonstrated, for example, by the reactions of primary perfluoropolyether iodides with bromobenzene which could lead directly to perfluoropolyether substituted bromobenzene without the use of toxic or pyrophoric chemicals such as sulfur tetrafluoride or butyl lithium. These functionalized perfluoropolyether (PFPE) intermediates are used to form readily soluble, high temperature additives for fluorinated oils in boundary lubrication, as disclosed in US Patent 5,550,277. These primary bromides or iodides described herein can also be used as intermediates in the production of fluorous phase media for applications such as catalysis (Horváth, I., Acc. Chem. Res. **1998**, 31, 641) or separations (Curran, D. P. Angew. Chem., Int. Ed. Engl. **1998**, 37, 1174.), fluorosurfactants, and mold release agents.

Because there are few useful perfluoropolyether primary bromides or iodides and processes for producing them are not readily available to one skilled in the art, there is an ever increasing need to develop such products and processes.

SUMMARY OF THE INVENTION

According to a first embodiment of the invention, a perfluoropolyether or a composition comprising thereof is provided, in which the perfluoropolyether comprises perfluoroalkyl radical end groups in which the radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and a 1,2-bis(perfluoromethyl)ethylene diradical, $-CF(CF_3)CF(CF_3)-$, is absent in the molecule of the perfluoropolyether.

According to a second embodiment of the invention, a process for improving the thermal stability of a perfluoropolyether is provided, which comprises modifying a process for producing a perfluoropolyether such that substantially all end groups of the perfluoropolyether have at least 3 carbon atoms per end group or, preferably, are C_3-C_6 branched and straight chain perfluoroalkyl end groups.

According to a third embodiment of the invention, a process is provided for producing a perfluoropolyether comprising perfluoroalkyl radical end groups

in which the perfluoroalkyl radical has at least 3 carbon atoms per radical as disclosed in the first embodiment of the invention. The process can comprise (1) contacting a perfluoro acid halide, a C_2 to C_4-substituted ethylene epoxide, a C_{3+} fluoroketone, or combinations of two or more thereof with a metal halide to produce an alkoxide; (2) contacting the alkoxide with either hexafluoropropylene oxide or 2,2,3,3-tetrafluorooxetane to produce a second acid halide; (3) esterifying the second acid halide to an ester; (4) reducing the ester to its corresponding alcohol; (5) converting the corresponding alcohol with a base to a salt form; (6) contacting the salt form with a C_3 or higher olefin to produce a fluoropolyether; and (7) fluorinating the fluoropolyether.

According to a fourth embodiment of the invention, a thermally stable grease or lubricant is provided, which comprises a thickener with a perfluoropolyether of composition thereof disclosed in the first embodiment of the invention.

According to a fifth embodiment of the invention, a perfluoropolyether and a composition comprising the perfluoropolyether are provided in which the perfluoropolyether comprises at least one halogen atom at the primary position of one or more end groups of the perfluoropolyether and the halogen atom is bromine or iodine.

Also provided is a process for producing the composition in which the process comprises contacting either (1) a perfluoropolyether acid fluoride with a metal bromide or metal iodide or (2) heating a perfluoropolyether secondary halide under a condition sufficient to effect the production of a perfluoropolyether comprising at least one bromine or iodine at the primary position of one or more end groups of the perfluoropolyether.

DETAILED DESCRIPTION OF THE INVENTION

This invention is directed to a thermal stable perfluoropolyether (or PFPE) composition and processes for making and using the composition. The term "perfluoropolyether" and "PFPE fluid" ("PFPE" or "PFPE fluids") are, unless otherwise indicated, exchangeable.

According to the first embodiment of the invention, there is provided a perfluoropolyether comprising branched or straight chain perfluoroalkyl radical end groups, each of which has at least 3 carbon atoms per radical, is substantially free of perfluoromethyl and perfluoroethyl end groups and does not contain any 1,2-bis(perfluoromethyl)ethylene diradicals [$-CF(CF_3)CF(CF_3)-$] in the chain. The term "substantially", as used herein, refers to a perfluoropolyether or PFPE fluid of this invention having only trace C_1-C_2 perfluoroalkyl endgroups such that the initial decomposition in a specific use is inconsequential and tolerable. An unavoidable trace of remaining perfluoropolyether or PFPE molecules with a perfluoro-methyl or -ethyl end group, while not desirable, may be tolerable as such molecules degrade to volatile products, leaving the more stable PFPE molecules. Thus thermal stability increases after some initial degradation.

The preferred perfluoropolyethers have the formula of $C_rF_{(2r+1)}$-A-$C_rF_{(2r+1)}$ in which each r is independently 3 to 6; if r = 3, both end groups $C_rF_{(2r+1)}$ are perfluoropropyl radicals; A can be $O-(CF(CF_3)CF_2-O)_w$, $O-(CF_2-O)_x(CF_2CF_2-O)_y$, $O-(C_2F_4-O)_x$, $O-(C_2F_4-O)_x(C_3F_6-O)_y$, $O-(CF(CF_3)CF_2-O)_x(CF_2-O)_y$, $O(CF_2CF_2CF_2O)_w$, $O-(CF(CF_3)CF_2-O)_x(CF_2CF_2-O)_y-(CF_2-O)_z$, or combinations of two or more thereof; preferably A is $O-(CF(CF_3)CF_2-O)_w$, $O-(C_2F_4-O)_x$, $O(C_2F_4O)_x(C_3F_6-O)_y$, $O-(CF_2CF_2CF_2-O)_x$, or combinations of two or more thereof; w is 4 to 100; x, y, and z are each independently 1 to 100.

Such compositions, as illustrated in the EXAMPLES section, show a significant increase in thermal stability over the corresponding PFPE fluids having perfluoroethyl or perfluoromethyl end groups. Similarly, stability of those PFPE fluids subject to degradation at the perfluoroalkyl terminal group, in addition to those based on poly(HFPO), can be improved by replacing $-CF_3$ and $-C_2F_5$ groups with, for example, C_3-C_6 perfluoroalkyl groups.

According to the second embodiment of the invention, a process for improving the thermal stability of a perfluoropolyether is provided. The process can comprise (1) incorporating one C_{3+} terminal segment into a perfluoropolyether precursor to produce a precursor having an initial C_{3+} end group; (2) polymerizing the precursor having an initial C_{3+} end group to a desired molecular weight polymer containing an alkoxide growing chain; (3)

incorporating a second C_{3+} end group to produce a polyether having both C_{3+} end groups; and (4) fluorinating the polyether having both C_{3+} end groups. The term "C_{3+}" refers to 3 or more carbon atoms.

Several processes are available for producing a PFPE fluid having improved thermal stability. The process is more fully disclosed in the third embodiment of the invention, other similar processes are evident to those skilled in the art. For example purposes, poly(HFPO) fluids are subject to exacting fractional distillation under vacuum. In practice, the upper molecular weight limit for such a distillation is the separation and isolation of $F(CF(CF_3)\text{-}CF_2\text{-}O)_9\text{-}CF_2CF_3$ and $F(CF(CF_3)\text{-}CF_2\text{-}O)_9\text{-}CF(CF_3)_2$. The increased thermal stability of free fluids with perfluoropropyl and perfluorohexyl end groups over those with perfluoroethyl end groups, described in the EXAMPLES, demonstrates the present invention.

The invention discloses perfluoropolyether having preferred C_3-C_6 perfluoroalkyl ether end groups. It is, however, within the scope of the invention that the disclosure is also applicable to any C_{3+} perfluoroalkyl ether end group. In the case of KRYTOX, for instance, the resultant poly(HFPO) chain terminates at both ends with C_3-C_6 perfluoroalkyl groups, having the formula of

$$C_rF_{(2r+1)}\text{-}O\text{-}[\text{-}CF(CF_3)\text{-}CF_2\text{-}O\text{-}]_s\text{-}C_rF_{(2r+1)} \qquad \text{(Formula 5)}$$

According to the third embodiment of the invention, a process for producing a preferred perfluoropolyether in which substantially all perfluoroalkyl end groups of the perfluoropolyether contain at least three, preferably 3 to 6, carbon atoms per end group. The preferred perfluoropolyether has the formula of $C_rF_{(2r+1)}\text{-}A\text{-}C_rF_{(2r+1)}$ as disclosed in the first embodiment of the invention. The process can comprise (1) contacting a perfluoro acid halide, a C_2 to C_4-substituted ethylene epoxide, a C_{3+} fluoroketone, or combinations of two or more thereof with a metal halide to produce an alkoxide; (2) contacting the alkoxide with either hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid fluoride; (3) contacting the second acid fluoride with an alcohol to produce an ester; (4) reducing the ester to corresponding alcohol: (5) contacting the corresponding alcohol with a base to a salt form; (6) contacting the salt form with

a C_{3+} or higher olefin to produce a fluoropolyether; and (7) fluorinating the fluoropolyether to produce the perfluoropolyether of the invention.

Typically, one C_{3+} terminal segment is produced first (the "initial end group") followed by its polymerization using, for example, hexafluoropropylene oxide or tetrafluorooxetane to a desired molecular weight polymer. This polymer is thermally treated to convert the growing alkoxide chain to an acid fluoride. The acid fluoride is converted to an ester, which is then reduced to its corresponding alcohol. The second C_{3+} terminal group (the "final end group") is now incorporated into the polymer by, for example, treatment with a mineral base in a suitable solvent and the addition of a reactive hydro- or fluoro-olefin. Reactive hydroolefins include allyl halides and tosylates. Finally the PFPE is formed by replacing essentially all hydrogen atoms with fluorine atoms.

Process 1 discloses a process for producing PFPEs terminated with paired normal C_3 to C_6 end groups. The process comprises (1) contacting a perfluoro acid halide or a C_2 to C_4-substituted ethylene epoxide with a metal halide to produce an alkoxide; (2) contacting the alkoxide with either hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting the second acid halide with an alcohol to produce an ester; (4) reducing the ester to corresponding alcohol: (5) contacting the corresponding alcohol with a base to a salt form; (6) contacting the salt form with a C_{3+} olefin to produce a fluoropolyether; and (7) fluorinating the fluoropolyether to produce the perfluoropolyether of the invention. The preferred halide, unless otherwise indicated, is fluoride and the preferred base is a metal hydroxide such as, for example, alkali metal hydroxide as used below to illustrate these steps.

Step 1 involves the contact of either a C_3-C_6 perfluoro acid fluoride or a C_2 to C_4 substituted ethylene epoxide with a metal fluoride, such as CsF or KF, in a suitable solvent such as tetraethylene glycol dimethyl ether at temperatures from about 0° to about 100°C to form an alkoxide which can be further polymerized.

$$R_f^4COF + MF \rightarrow R_f^4CF_2O^- M^+$$

$$\underset{\diagdown\;O\;\diagup}{R_f^1\text{-}CF\text{—}CF_2} + MF \rightarrow R_f^1CF_2CF_2O^- M^+,$$

where preferred M is a metal such as cesium or potassium, R_f^4 is $C_aF_{(2a+1)}$, a is 2 to 5, R_f^1 is $C_bF_{(2b+1)}$, and b is 1 to 4.

Step 2 involves the contact of the alkoxide with either hexafluoropropylene oxide or tetrafluorooxetane at low temperature, about -30 to about 0 °C, followed by thermolysis at >50 °C, to produce the PFPE with one C_3-C_6 end group and an acid fluoride on the other terminus, and having the Formula 6 (from HFPO) or Formula 7 (from tetrafluorooxetane).

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)COF$ (Formula 6)

or $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2COF$, (Formula 7)

The (C_3-C_6 Segment) is defined C_3-C_6 perfluoroalkyl group having an oxygen between the segment and the polymer repeat unit.

Alternatively, Formula 7 can be converted to an equivalently useful acid fluoride by replacing all methylene hydrogen radicals with fluorine radicals using the fluorination procedure disclosed in Step 7, with or with out the use of a suitable solvent, at temperatures of about 0 to about 180 °C, and with autogenous or elevated fluorine pressures of 0 to 64 psig (101 to 543 kPa). The resulting perfluorinated acid fluoride is then further processed as follows.

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2COF + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CF_2CF_2CF_2O)_sCF_2CF_2COF$.

Step 3 involves the contact of the acid fluoride with an alcohol such as methanol, with or without solvent or excess alcohol, at a temperature of about 0 to about 100 °C, producing the corresponding ester. The HF produced can be removed by washing with water.

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)COF + R^1OH \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)COOR^1$,

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2COF + R^1OH \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2COOR^1$,
where R^1 is alkyl and preferably methyl.

In Step 4, the ester is reduced with a reducing agent such as, for example, sodium borohydride or lithium aluminum hydride in a solvent such as an alcohol or THF (tetrahydrofuran) at a range of temperatures (0 to 50 °C) and at autogenous pressure for a time period of from about 30 minutes to about 25 hours to produce the corresponding alcohol (PFPE precursor):

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)COOR^1 + NaBH_4 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OH$,
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2COOR^1 + NaBH_4 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OH$.

In Step 5, the PFPE precursor alcohol is converted to a metal salt. The conversion can be effected by contacting the precursor alcohol with a metal hydroxide, optionally in a solvent, under a condition sufficient to produce the metal salt. The presently preferred metal hydroxide includes alkali metal hydroxides such as, for example, potassium hydroxide and alkaline earth metal hydroxides. Any solvent, such as, for example, acetonitrile, that does not interfere with the production of the metal salt can be used. Suitable condition include a temperature in the range of from about 20 to about 100 °C under a pressure of about 300 to about 1,000 mmHg (40 - 133 kPa) for about 30 minutes to about 25 hours.

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OH + M^1OH \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OM^1$,

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OH + M^1OH \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OM^1$,
where M^1 is an alkali metal, an alkaline earth metal, or ammonium.

In Step 6, the metal salt is contacted with an olefin to produce a C_3 - C_6 segment fluoropolyether. The contacting can be carried out in the presence of a solvent such as, for example, an ether or alcohol, under a condition to produce a fluoropolyether that can be converted to perfluoropolyether of the invention by fluorination disclosed herein below. Any olefin having more than three carbon atoms, preferably 3 to 6, can be used. The olefin can also be substituted with, for example, a halogen. Examples of such olefins include, but are not limited to, hexafluoropropylene, octafluorobutene, perfluorobutylethylene, perfluoroethylethylene, perfluorohexene, allyl halides, and combinations of two or more thereof. Additionally, a C_3 - C_6 segment containing a moiety known in the art to be a good leaving group in nucleophilic displacement reactions, for example tosylates, can also be used. The contacting conditions can include a temperature in the range of from about 0 to about 100 °C under a pressure in the range of from about 0.5 to about 64 psig (105 - 543 kPa) for about 30 minutes to about 25 hours.

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OM^1 + R_f^1CF{=}CF_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF_2CFHR_f^1 +$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF{=}CFR_f^1$; or

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)\ CH_2OM^1 + X^1CHR^2CH{=}CH_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH{=}CHR^2$ where R^2 is $C_cH_{(2c+1)}$, c is 0 to 3, and X^1 is a halogen; or

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OM^1 + R_f^5CF_2CH{=}CH_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH_2CF_2R_f^5 +$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH{=}CFR_f^5$ where R_f^5 is $C_cF_{(2c+1)}$; or

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OM^1 + R_f^1CF{=}CF_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCF_2CFHR_f^1 +$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCF{=}CFR_f^1$; or

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OM^1 + X^1CHR^2CH{=}CH_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH{=}CHR^2$; or

$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OM^1 + R_f^5CF_2CH{=}CH_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH_2CF_2R_f^5 +$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH{=}CFR_f^5.$

In Step 7, the perfluoropolyether with paired C_3 to C_6 segments is formed with elemental fluorine using any technique known to one skilled in the art such as disclosed in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 11, page 492 and references therein.

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF_2CFHR_f^1 +$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF{=}CFR_f^1 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2R_f^1$; or
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH{=}CHR^2 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2CF_2R_f^5$; or
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH_2CF_2R_f^5 +$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH{=}CFR_f^1 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2CF_2R_f^5$; or
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCF_2CFHR_f^1 +$
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCF{=}CFR_f^1 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CF_2CF_2CF_2O)_sCF_2CF_2CF_2OCF_2CF_2R_f^1$; or
$(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH{=}CHR^2 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CF_2CF_2CF_2O)_tCF_2CF_2CF_2OCF_2CF_2CF_2R_f^5$; or

$(C_3\text{-}C_6 \text{ SEGMENT})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH_2CF_2R_f^5 +$
$(C_3\text{-}C_6 \text{ SEGMENT})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OCH_2CH{=}CFR_f^5 + F_2 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(CF_2CF_2CF_2O)_tCF_2CF_2CF_2OCF_2CF_2CF_2R_f^5.$

Process 2 discloses the synthesis of PFPEs terminated with a normal C_3 to C_6 initial end group and a branched C_3 to C_6 final end group. Steps 1 to 5 are the same as those in Process 1. The terminal fluoroalkene or allyl halide in Step 6 is replaced with a branched fluoroalkene such as 2-perfluorobutene or a branched allyl halide such as 1-bromo-2-butene. Step 7 is as described in Process 1.

$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OH + M^1OH + R_f^6CF{=}CFR_f^7 \rightarrow$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF(R_f^6)CFHR_f^7 +$
$(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OC(R_f^6){=}CFR_f^7$ where R_f^6 is $C_eF_{(2e+1)}$, R_f^7 is $C_fF_{(2f+1)}$, such that e and $f \geq 0$, $(e + f) \leq 4$ and $(e + f) \geq 1$; or

$(C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)CH_2OH + M^1OH + X^1CR^4CH{=}CHR^5 \rightarrow (C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)CH_2OCH(R^5)CH{=}CHR^4$ where R^4 is $C_gH_{(2g+1)}$, R^5 is $C_hH_{(2h+1)}$, such that g and h ≥ 0 and $(g + h)$ is 1 to 3.

Process 3A discloses the synthesis of PFPEs terminated with a branched C_3 to C_6 initial end group and a normal C_3 to C_6 final end group. The reagents, either the acid fluoride or epoxide, in Step 1 of Process 1, are replaced with a C_3 to C_6 fluoroketone. Then, steps 2 to 7 of Process 1 are used.

$R_f^8C(O)R_f^9 + MF \rightarrow R_f^8(R_f^9)CFO^- M^+$,

where R_f^8 is $C_jF_{(2j+1)}$, R_f^9 is $C_kF_{(2k+1)}$, such that j and k ≥ 1, $(j + k) \leq 5$.

Process 3B discloses the synthesis of PFPEs terminated with paired branched C_3 to C_6 end groups. Step 1 of Process 3 is practiced, followed by Steps 2 to 5 of Process 1, followed by Step 6 of Process 2A, and then finally Step 7 of Process 1.

Process 4 discloses the synthesis of PFPEs terminated with a C_3 to C_6 initial end group and a C_3 to C_6 final end group. Steps 1 to 3 of Process one; or Steps 1 of Process 3A and steps 2 and 3 of Process 1 are followed. The ester is then contacted with a Grignard Reagent of the type $C_2H_5M^2X^1$ or $CH_3M^2X^1$, where M^2 is magnesium or lithium, forming the carbinol which can either be dehydrated or fluorinated directly in Step 7 as described in Process 1 to the desired PFPE. Steps 4 through 6 disclosed in Process 1 are omitted.

$(C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)C(O)OR^1 + 2R^6M^2X^1 \rightarrow (C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)C(OH)(R^6)_2$,

$(C_3\text{-}C_6\ \text{Segment})(CH_2CF_2CF_2O)_tCH_2CF_2COOR^1 + 2R^6M^2X^1 \rightarrow (C_3\text{-}C_6\ \text{Segment})(CH_2CF_2CF_2O)_tCH_2CF_2C(OH)(R^6)_2$,

where R^6 is CH_3 or C_2H_5 such that the total number of carbons in the final segment is 3 to 6 and $(R^6)_2$ always means no more than one CH_3 and one C_2H_5.

Alternatively, $(C_3\text{-}C_6\ \text{Segment})(CF_2CF_2CF_2O)_tCF_2CF_2COOR^1 + 2R^6M^2X^1 \rightarrow (C_3\text{-}C_6\ \text{Segment})(CF_2CF_2CF_2O)_tCF_2CF_2C(OH)(R^6)_2$.

Process 5 discloses an additional procedure for making PFPEs with a C_3-C_6 initial end group with a branched or normal C_3-C_6 final end group, which comprises (1) contacting a PFPE acid fluoride precursor prepared in steps 1 and 2

of Process 1 or steps 1 and 2 of Process 3 with a metal iodide such as, for instance, lithium iodide at an elevated temperatures such as, for example, at least 180 °C, or at least 220 °C, to produce a corresponding iodide; (2) either replacing the iodine radical with a hydrogen radical using a suitable reducing agent such as, for example, sodium methylate at temperatures of about 25 °C to about 150 °C and autogenous pressure alone or reacting said iodide with a C_2 to C_4 olefin using a peroxide or azo catalyst or zero valent metal catalyst, or dehydrohalogenating the iodide/olefin adduct in alcoholic solvent; and (3) fluorinating the corresponding products to produce the desired perfluoropolyether.

Process 5 Step 1

(C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)COF + LiI → (C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)I + LiF + CO,

(C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$COF + LiI → (C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$I + LiF + CO,

{R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_s$CF(CF$_3$)COF + LiI → {R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_s$CF(CF$_3$)I + LiF + CO;

(C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)COF + LiI → (C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$I + CF$_3$COF + LiF + CO;

{R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_s$CF(CF$_3$)COF + LiI → {R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$I + CF$_3$COF + LiF + CO.

Process 5 Step 2A

(C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)I + CX$_2$=CXR^7 → (C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)CX$_2$CXIR^7 where X = H or F, R^7 = C$_d$X$_{(2d+1)}$, d = 0 to 2;

(C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$I +CX$_2$=CXR^7 → (C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$CX$_2$CXIR^7;

{R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_s$CF(CF$_3$)I + CX$_2$=CXR^7 → {R$_f^8$(R$_f^9$)CFO Segment}(HFPO)$_s$CF(CF$_3$)CX$_2$CXIR^7;

(C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$) CF$_2$I + CX$_2$=CXR^8 → (C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CX$_2$CXIR^8 where R^8 = C$_v$X$_{(2v+1)}$, v = 0 to 1;

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2I + CX_2{=}CXR^8 \rightarrow$
$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2CX_2CXIR^8$.

Process 5 Step 2A1, when one X of the terminal methylene from the olefin of process 5 Step 2A was Hydrogen.

$(C_3\text{-}C_6\ Segment)(HFPO)_sCF(CF_3)CX_2CXIR^7 + M^1OH \rightarrow$
$(C_3\text{-}C_6\ Segment)\ (HFPO)_sCF(CF_3)CX{=}CXR^7$; or

$(C_3\text{-}C_6\ Segment)(CF_2CF_2CF_2O)_sCF_2CF_2CX_2CXIR^7 + M^1OH \rightarrow$
$(C_3\text{-}C_6\ Segment)(CF_2CF_2CF_2O)_sCF_2CF_2CX{=}CXR^7$; or

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_sCF(CF_3)CX_2CXIR^8 + M^1OH \rightarrow$
$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_sCF(CF_3)CX{=}CXR^8$; or

$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_2CX_2CXIR^8 + M^1OH \rightarrow$
$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_2CX{=}CXR^8$; or

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2CX_2CXIR^8 + M^1OH \rightarrow$
$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2CX{=}CXR^8$.

Process 5 Step 2B

$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_2I + NaOCH_3/HOCH_3 \rightarrow$
$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_2H$, or

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2I + NaOCH_3/HOCH_3 \rightarrow$
$\{R_f^8(R_f^9)CO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2H$.

Process 5 Step 3A

$(C_3\text{-}C_6\ Segment\ (HFPO)_{(s-1)}CF(CF_3)CF_2I + F_2 \rightarrow$
$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_3$; or

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2I + F_2 \rightarrow$
$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_3$.

Process 5 Step 3B

$(C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_2H + F_2 \rightarrow (C_3\text{-}C_6\ Segment)(HFPO)_{(s-1)}CF(CF_3)CF_3$; or

$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_2H + F_2 \rightarrow$
$\{R_f^8(R_f^9)CFO\ Segment\}(HFPO)_{(s-1)}CF(CF_3)CF_3$.

Process 5 Step 3C

(C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CX$_2$CXIR^7 + F$_2$ → (C$_3$-C$_6$ Segment)(HFPO)$_s$CF(CF$_3$)CF$_2$CF$_2$ R$_f^{10}$, where R$_f^{10}$= C$_d$F$_{(2d+1)}$, or

(C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$CX$_2$CXIR^7+ F$_2$→ (C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$CF$_2$CF$_2$R$_f^{10}$; or

{R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_s$CF(CF$_3$)CX$_2$CXIR^7 + F$_2$ → {R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_s$CF(CF$_3$)CF$_2$CF$_2$R$_f^{10}$;or

(C$_3$-C$_6$ Segment)(HFPO) $_{(s-1)}$CF(CF$_3$)CF$_2$CX$_2$CXIR^8 + F$_2$ → (C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CF$_2$CF$_2$R$_f^{11}$ where R$_f^{11}$ = C$_v$F$_{(2v+1)}$, or

{R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CX$_2$CXIR^8 + F$_2$ → {R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CF$_2$CF$_2$R$_f^{11}$.

Process 5 Step 3D

(C$_3$-C$_6$ Segment)(HFPO)$_{(s)}$CF(CF$_3$)CX=CXR^7 + F$_2$ → (C$_3$-C$_6$ Segment)(HFPO)$_{(s)}$CF(CF$_3$)CF$_2$CF$_2$ R$_f^{10}$; or

(C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$CX=CXR^7+ F$_2$→ (C$_3$-C$_6$ Segment)(CF$_2$CF$_2$CF$_2$O)$_t$CF$_2$CF$_2$CF$_2$CF$_2$R$_f^{10}$; or

{R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_s$CF(CF$_3$)CX=CXR^7 + F$_2$ → {R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_s$CF(CF$_3$)CF$_2$CF$_2$R$_f^{10}$; or

(C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CX=CXR^8 + F$_2$ → (C$_3$-C$_6$ Segment)(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CF$_2$CF$_2$R$_f^{11}$, or

{R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CX=CXR^8 + F$_2$ → {R$_f^8$(R$_f^9$)CO Segment}(HFPO)$_{(s-1)}$CF(CF$_3$)CF$_2$CF$_2$CF$_2$R$_f^{11}$.

Process 6 discloses the synthesis of PFPEs terminated with C$_3$-C$_6$ end groups by the fluorination of corresponding hydrocarbon polyethers, following the process described in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 11. pages 492 and specifically as described by Bierschenk et al. in US Patents 4,827,042, 4,760,198, 4,931,199, and 5,093,432, and using the suitable starting materials with the proper end groups, compositions disclosed can be prepared.

The hydrocarbon polyether can be combined with an inert solvent such as 1,1,2-trichlorotrifluoroethane to produce a fluorination mixture, optionally in the presence of a hydrogen fluoride scavenger such as sodium or potassium fluoride.

A fluid mixture containing fluorine and an inert diluent such as nitrogen can be introduced to the fluorination mixture for a sufficient period of time to convert essentially all hydrogen atoms to fluorine atoms. The flow rate of the fluid can be in the range of from about 1 to about 25000 ml/min, depending on the size of the fluorination mixture. The fluoropolyether can also be introduced after the introduction of the fluorine-containing fluid at a rate such that a perfluorination of the fluoropolyether can be accomplished.

$C_rH_{(2r+1)}O\text{-}(CH(CH_3)CH_2\text{-}O)_wC_rH_{(2r+1)} + F_2 \rightarrow C_rF_{(2r+1)}O\text{-}(CF(CF_3)CF_2\text{-}O)_wC_rF_{(2r+1)}$;

$C_rH_{(2r+1)}O\text{-}(C_2H_4\text{-}O)_wC_rH_{(2r+1)} + F_2 \rightarrow C_rF_{(2r+1)}O\text{-}(C_2F_4\text{-}O)_wC_rF_{(2r+1)}$;

$C_rH_{(2r+1)}O\text{-}(C_2H_4\text{-}O)_w(C_3H_6\text{-}O)_wC_rH_{(2r+1)} + F_2 \rightarrow C_rF_{(2r+1)}O\text{-}(C_2F_4\text{-}O)_w(C_3F_6\text{-}O)_wC_rF_{(2r+1)}$;

$C_rH_{(2r+1)}O\text{-}(CH_2CH_2CH_2\text{-}O)_w(CH(CH_3)CH_2\text{-}O)_uC_rH_{(2r+1)} + F_2 \rightarrow C_rF_{(2r+1)}O\text{-}(CF_2CF_2CF_2\text{-}O)_w(CF(CF_3)CF_2\text{-}O)_uC_rF_{(2r+1)}$ where u is 0 to 100.

Process 7 discloses the synthesis of PFPEs terminated with a C_3 to C_6 initial end group and a branched C_3 final end group. The reagents are those described in steps 1 to 4 of Process 1, or in step 1 of Process 3, followed by steps 2 to 4 of Process 1 to provide a starting alcohol. An alcohol having either branched or normal starting end can be reacted with sulfur tetrafluoride (SF_4) or a derivative of SF_4 such as N,N,-diethylaminosulfur trifluoride or a phosphorus pentahalide PX^2_5 such as phosphorous pentabromide, where X^2 is Br, Cl, or F at temperatures of about 25 to about 150 °C and autogenous pressure with or without solvent gives the terminal dihydrohalide which can be fluorinated according to step 7 of process 1, as illustrated below.

$(C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)CH_2OH + SF_4 \rightarrow (C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)CH_2F$,

$(C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)CH_2F + F_2 \rightarrow (C_3\text{-}C_6\ \text{Segment})(HFPO)_sCF(CF_3)_2$,

$\{R_f^8(R_f^9)CFO\ \text{Segment}\}(HFPO)_sCF(CF_3)CH_2OH + SF_4 \rightarrow \{R_f^8(R_f^9)CFO\ \text{Segment}\}(HFPO)_sCF(CF_3)CH_2F$;

$\{R_f^8(R_f^9)CFO\ \text{Segment}\}(HFPO)_sCF(CF_3)CH_2F + F_2 \rightarrow \{R_f^8(R_f^9)CFO\ \text{Segment}\}(HFPO)_sCF(CF_3)_2$.

$(C_3\text{-}C_6\ \text{Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2OH + SF_4 \rightarrow$
$(C_3\text{-}C_6\ \text{Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2F$
$(C_3\text{-}C_6\ \text{Segment})(CH_2CF_2CF_2O)_tCH_2CF_2CH_2F + F_2 \rightarrow$
$(C_3\text{-}C_6\ \text{Segment})(CF_2CF_2CF_2O)_tCF_2CF_2CF_3$

Process 8 discloses the synthesis of PFPEs terminated with a C_3 to C_6 initial end group and specifically a perfluorotertiary final end group. Here, either a salt of any fluorotertiary alcohol such as perfluoro-t-butanol, or perfluoro-t-butyl hypofluorite is reacted with any fluoropolyether with a starting C_3-C_6 or $R_f^8(R_f^9)CFO$ segment and either a $-A-O-C(CF_3)=CF_2$ or $-A-O-C(CF_3)=CHF$ terminus as shown. The resulting product is then fluorinated, if necessary.

$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}C(CF_3)=CF_2 + M^1OC(CF_3)_3 \rightarrow$
$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}CH(CF_3)CF_2OC(CF_3)_3,$
$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}CH(CF_3)CF_2OC(CF_3)_3 + F_2 \rightarrow$
$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}CF(CF_3)CF_2OC(CF_3)_3,$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}C(CF_3)=CF_2 + M^1OC(CF_3)_3 \rightarrow$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}CH(CF_3)CF_2OC(CF_3)_3,$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}CH(CF_3)CF_2OC(CF_3)_3 + F_2 \rightarrow$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}CF(CF_3)CF_2OC(CF_3)_3,$
$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}C(CF_3)=CF_2 + FOC(CF_3)_3 \rightarrow$
$(C_3\text{-}C_6\ \text{Segment})\text{-}A\text{-}O\text{-}CF(CF_3)CF_2OC(CF_3)_3,$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}C(CF_3)=CF_2 + FOC(CF_3)_3 \rightarrow$
$\{R_f^8(R_f^9)CFO\ \text{Segment}\}\text{-}A\text{-}O\text{-}CF(CF_3)CF_2OC(CF_3)_3$

While the procedures for replacing end groups with C_3 - C_6 end groups can also be practiced on the FOMBLIN fluids described above, the value of inserting the more stable end groups is severely limited due to the presence of the chain destabilizing $-O-CF_2-O-$ segments therein.

The PFPE fluids of the invention can be purified by any means known to one skilled in the art such as contact with absorbing agents, such as charcoal or alumina, to remove polar materials and fractionated conventionally by distillation under reduced pressure by any method known to one skilled in the art.

According to the fourth embodiment of the invention, a thermally stable grease or lubricant composition is provided. Greases containing the perfluoropolyether disclosed in the first embodiment of the invention can be produced by combining the perfluoropolyether with a thickener. Examples of such thickeners include, but are not limited to, standard thickeners such as, for example, poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof. The thickeners can be present in any appropriate particle shapes and sizes as known to one skilled in the art.

According to the invention, the perfluoropolyether of the invention can be present in the composition in the range of from about 0.1 to about 50, preferably 0.2 to 40, percent by weight. The composition can be produced by any methods known to one skilled in the art such as, for example, by blending the perfluo

According to the fifth embodiment of the invention, examples of the perfluoropolyether primary bromide or iodide include, but are not limited to, those having the formulae of $F(C_3F_6O)_{z'}CF(CF_3)CF_2X$, , $X(CF_2)_{a'}(CF_2O)_{m'}(CF_2CF_2O)_{n'}(CF_2)_{a'}X$, $F(C_3F_6O)_{x'}(CF_2O)_{m'}CF_2X$, $F(C_3F_6O)_{x'}(C_2F_4O)_{n'}(CF_2O)_{m'}CF_2X$, $XCF_2CF(CF_3)O(C_3F_6O)_{p'}R_f^{2'}O(C_3F_6O)_{n'}CF(CF_3)CF_2X$, $XCF_2CF_2O(C_3F_6O)_{x'}CF(CF_3)CF_2X$, $(R_f^{1'})(R_f^{1'})CFO(C_3F_6O)_{x'}CF(CF_3)CF_2X$, and combinations of two or more thereof where X is I or Br, x' is a number from 2 to about 100, z' is a number from about 5 to about 100, p' is a number from 2 to about 50, n' is a number from 2 to about 50, m' is a number from 2 to about 50, a is 1 or 2, each $R_f^{1'}$ can be the same or different and is independently a monovalent C_1 to C_{20} branched or linear fluoroalkanes, $R_f^{2'}$ is a divalent C_1 to C_{20} branched or linear fluoroalkanes, and C_3F_6O is linear or branched.

The composition of the invention can be produced by any means known to one skilled in the art. It is preferred that it be produced by the process disclosed herein.

According to the invention, a process for producing the composition disclosed above can comprise, consist essentially of, or consist of contacting either (1) a perfluoropolyether acid fluoride or diacid fluoride containing a COF moiety with a metal bromide or metal iodide or (2) heating a perfluoropolyether

secondary halide under a condition sufficient to effect the production of a perfluoropolyether comprising at least one bromine or iodine at the primary position of one or more end groups of the perfluoropolyether. The process generally involves a β-scission reaction. The process is preferably carried out under a condition or in a medium that is substantially free of a solvent or iodine or both. The process can also be carried out substantially free of a metal salt that is not a metal halide.

The acid fluoride including monoacid fluoride and diacid fluoride of formula I and II, respectively, can be contacted with a metal iodide such as lithium iodide, calcium iodide, or barium iodide to make either a secondary or primary perfluoropolyalkylether iodide with the evolution of carbon monoxide and formation of the metal fluoride according to Reaction 1 for the monofunctional acid fluoride and Reaction 2 for the difunctional acid fluoride. These reactions can be carried out at or above about 180 °C, preferably at or above about 220 °C.

Reaction 1:

$\Phi\text{-}CF(CF_3)CF_2OCF(CF_3)C(O)\text{-}F + M_{(1/v')}I \rightarrow$

$\Phi\text{-}CF(CF_3)CF_2\text{-}I + M_{(1/v')}F + CO + CF_3C(O)F$

Reaction 2:

$FC(O)CF(CF_3)OCF_2CF(CF_3)\text{-}\Phi'\text{-}CF(CF_3)CF_2OCF(CF_3)C(O)F + 2M_{(1/v')}I \rightarrow$

$ICF_2CF(CF_3)\text{-}\Phi'\text{-}CF(CF_3)CF_2I + 2M'_{(1/v')}F + 2CO + 2CF_3C(O)F$

wherein Φ, Φ' are as previously described, M' is a metal selected from Li, Ca, or Ba, and v' is the valency of the metal M'.

A perfluoropolyether acid fluoride containing a $-CF_2OCF(CF_3)COF$ moiety can be combined with a metal bromide or metal iodide under a condition sufficient to effect the production of a perfluoropolyether primary bromide or iodide. The metal moiety can be an alkali metal, an alkaline earth metal, or combinations of two or more thereof. Examples of suitable metal bromide and metal iodide include but are not limited to, lithium iodide, calcium iodide, barium iodide, aluminum iodide, boron iodide, aluminum bromide, boron bromide, and combinations of two or more thereof. The conditions can include an elevated

temperature such as, for example, at or above about 180 °C, preferably at or above about 220 °C, under a pressure that can accommodate the temperature for a sufficient time period such as, for example, about 1 hour to about 30 hours.

The process can also comprise contacting a perfluoropolyether acid fluoride containing a COF moiety in the secondary position such as, for example, $CF(CF_3)CF_2OCF(CF_3)COF$, with a bromide or iodide M'X under the conditions disclosed above.

According to the invention, the perfluoropolyether that can be used in the process of the invention can also comprise repeat units derived from the group consisting of $-CF_2O-$, $-CF_2CF_2O-$, $-CF_2CF(CF_3)O-$, $-CF(CF_3)O-$, $-CF(CF_3)CF_2O-$, $-CF_2CF_2CF_2O-$, $-CF(CF_s)O-$, $-CF_2CF(CF_s)O-$, $-CF_2CF(CF_2CF_3)O-$, $-CF_2CF(CF_2CF_2CF_3)O-$, $-CF(CF_2CF_3)O-$, $-CF(CF_2CF_2CF_3)O-$, $-CH_2CF_2CF_2O-$, $-CF(Cl)CF_2CF_2O-$, $-CF(H)CF_2CF_2O-$, $CCl_2CF_2CF_2O-$, $-CH(Cl)CF_2CF_2O-$, and combinations of two or more thereof.

Perfluoropolyether containing these repeat units are well known to one skilled in the art. For example, KRYTOX available from E. I. du Pont de Nemours and Company comprises the repeat units of $-CF(CF_3)CF_2O-$.

The following examples illustrate the invention process.

$F(C_3F_6O)_{z'}CF(CF_3)CF_2OCF(CF_3)I \rightarrow F(C_3F_6O)_{z'}CF(CF_3)CF_2I$ (monofunctional), or $ICF(CF_3)OCF_2CF(CF_3)O(C_3F_6O)_{p'}R_f^{2'}O(C_3F_6O)_{n'}CF(CF_3)CF_2OCF(CF_3)I \rightarrow ICF_2CF(CF_3)O(C_3F_6O)_{p'}R_f^{2'}O(C_3F_6O)_{n'}CF(CF_3)CF_2I$ (difunctional).

PFPE primary iodides can also be converted to their respective PFPE primary bromides by contacting them with carbon tetrabromide, for example, at 180 °C according to

$$F(C_3F_6O)_{z'}CF(CF_3)CF_2I + CBr_4 \rightarrow F(C_3F_6O)_{z'}CF(CF_3)CF_2Br + \tfrac{1}{2}I_2 + \tfrac{1}{2}C_2Br_6$$

PFPE acid fluorides can also be converted to their respective acid bromides by contacting them with mixed metal bromides such as, for example, aluminum bromide mixed with boron bromide. The acid bromide can be isolated. The isolated acid bromide can be heated at elevated temperature such as, for example, about 340 °C.

EXAMPLES

Example 1 and Comparative Examples A and B.

Separation of $F[CF(CF_3)CF_2O]_6CF(CF_3)_2$ (IPA-F, Example 1), $F[CF(CF_3)$-CF_2-$O]_6$-CF_2CF_3 (EF, Comparative Example A) and $F[CF(CF_3)$-CF_2-$O]_7$-CF_2CF_3 (EF, Comparative Example B) from KRYTOX® Fluid ($F[CF(CF_3)$-CF_2-$O]_l$-R_f, l = 3-11) by Fractional Distillation.

Samples for the aforementioned Examples were obtained via successive fractional vacuum distillations of KRYTOX Heat Transfer Fluids. In the first distillation, a 100-cm long, 3-cm ID (inner diameter) column was used. The column was packed with Raschig rings made from 1/4" OD (outer diameter)/3/16" ID FEP (fluorinated ethylene polypropylene) tubing (obtained from Aldrich, Milwaukee, Wisconsin) cut into pieces about 1/4" long. The distillation was carried out under dynamic vacuum conditions, and a pure sample of $F[CF(CF_3)$-CF_2-$O]_7$-CF_2CF_3 (Comparative Example B) (approximately 350 g) was obtained at an overhead temperature of 88 - 92°C as a fraction. At this point, previous fractions were combined and fluorinated with elemental fluorine at 100°C in the presence of NaF in order to totally remove any hydrogen containing materials prior to the second distillation.

For the second distillation, a 120-cm long, 2.4-cm ID column packed with 1/4" Monel saddle-shaped packing was used. This distillation was again carried out under dynamic vacuum (about 20 mTorr, 2.7 kPa), and pure samples of $F[CF(CF_3)$-CF_2-$O]_6$-CF_2CF_3 (Comparative Example A) with an overhead temperature of 68 - 72°C (200 g) and $F[CF(CF_3)$-CF_2-$O]_6$-$CF(CF_3)_2$ (Example 1) with an overhead temperature of 72 - 73°C (85 g) were collected.

Example 2.

This example illustrates the production of a perfluoropolyether having paired perfluoro-n-propyl end groups.

Addition of Hexafluoropropene (HFP) to a Perfluoropolyether Alcohol

$$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OH + CF_2{=}CFCF_3 \rightarrow$$

$$F[CF(CF_3)CF_2O]_6CF(CF_3)CH_2OCF_2CHFCF_3$$

A perfluoropolyether alcohol (KRYTOX alcohol, available from E.I. du Pont de Nemours and Company, Wilmington, Delaware; 100.00 g) was added to a 250-

ml round-bottomed flask. Acetonitrile (160 ml) and finely ground potassium hydroxide (4.87 g, 86.8 mmol) was then added to the flask with a magnetic stir bar to make a reaction mixture. Once the flask was connected to a vacuum line, the mixture was degassed. Upon vigorous stirring, the reaction mixture was heated to 60 °C. When the temperature reached 60 °C, a constant pressure of 650 mmHg (87 kPa) of hexafluoropropene was applied to the same flask. Stirring and applied pressure was maintained until the reaction did not take up any more hexafluoropropene. A color change was observed during the reaction from a light yellow to a dark orange when the reaction was completed. After the reaction, water was added to the reaction mixture and the bottom layer was removed via a separatory funnel. This was done three times to insure a clean product. Lastly, any solvent in the fluorous product layer was stripped by vacuum. Final mass of product, a perfluoropolyether-alcohol HFP adduct, was 97.77 g (86.5% yield).

Fluorination of Perfluoropolyether-alcohol HFP Adduct

$$F[CF(CF_3)CF_2O]_6CF(CF_3)CH_2OCF_2CHFCF_3 + 20\%\ F_2 / 80\%\ N_2 \rightarrow$$

$$F[CF(CF_3)CF_2O]_7O(CF_2)_2CF_3$$

1,1,2-Trichlorotrifluoroethane (500 ml) and potassium fluoride (13.13 g, 22.6 mmol) were added to a fluorination reactor. Upon addition, the reactor was quickly closed and purged with dry nitrogen for 30 min at a rate of 300 ml/min. Next, the reactor was purged with 20% fluorine / 80% nitrogen for 30 min at a flow of 250 ml/min. The perfluoropolyether-alcohol HFP adduct (97.77g) was then added to the reactor via a pump at a rate of 0.68 ml/min with 480-490 ml/min flow of 20% fluorine, at a reactor stir rate of 800 rpm and a temperature of 25-28 °C for 76 min. In the next 30 min, the pump line was washed with an additional 20 ml of 1,1,2-trichlorotrifluoroethane. After a 106 min run time, the flow of fluorine was reduced to 250 ml/min for the next 60 min and then 40 ml/min with a stir rate of 600 rpm for the next 2 days. After the reaction, the system was purged with nitrogen. The product was removed and washed with water. The bottom layer was removed with a separatory funnel and the 1,1,2-trichlorotrifluoroethane was stripped from the product via the vacuum line. Final mass of the product was 91.96 g.

Example 3A.

This example illustrates the production of a perfluoropolyether having an initial perfluoro-n-propyl end group and a final perfluoro-n-hexyl end group.

Addition of 1-Perfluorohexene to a Perfluoropolyether Alcohol

$$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OH + (H_3C)_2CHO^- Na^+ \rightarrow F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2ONa \quad (1)$$

$$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2ONa + CF_2{=}CF(CF_2)_3CF_3 \rightarrow F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OCF{=}CF(CF_2)_3CF_3 + F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OCF_2\text{-}CHF(CF_2)_3CF_3 \quad (2)$$

A perfluoropolyether alcohol, KRYTOX alcohol (available from E. I. du Pont de Nemours and Company, Wilmington, Delaware; 74.6 g) was added to a 500-ml round-bottomed flask containing 6.25 g $(H_3C)_2CHONa$. After the colorless solid dissolved under stirring with the KRYTOX alcohol the iso-propanol byproduct was removed under vacuum yielding 76.3 g liquid sodium salt (100% yield). The flask was cooled with liquid nitrogen and anhydrous acetonitrile (88 g) and perfluoro-1-hexene (24.0 g) were then added to the flask by vacuum transfer. After reaching room temperature the mixture was stirred to start a mildly exothermic reaction. After the reaction, the acetonitrile and un-reacted C_6F_{12} were removed leaving 93.6 g of a non-volatile residue. The weight increase (17.3 g) indicated a 75.7% yield of crude product. Aqueous ammonium chloride solution was added to the reaction mixture, which was subsequently transferred into a separatory funnel. Phase separation was accomplished by adding a small amount of acetone and prolonged heating of the funnel to 90 °C. The lower layer was drained into a 250-ml round-bottomed flask and vacuum distilled via a 12 cm Vigreux column. 56.3 g of a mixture of saturated and unsaturated products were isolated.

Fluorination of Perfluoropolyether-alcohol Perfluorohexene Adducts

$$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OCF{=}CF(CF_2)_3CF_3 + F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OCF_2\text{-}CHF(CF_2)_3CF_3 + F_2\ (20\%)\ /\ N_2\ (80\%) \rightarrow F[CF(CF_3)\text{-}CF_2O]_6(CF_2)_5CF_3$$

The products of the above procedure were combined in a FEP (FEP fluoropolymer, a tetrafluoroethylene/hexafluoropropylene copolymer) tube reactor (O.D. 5/8 in [1.6 cm]) equipped with an FEP dip-tube and treated with 20% F_2 / 80% N_2 at ambient temperature at a rate of ca. 30 ml/min for 2 days at which time the contents were transferred to a 300 ml stainless steel cylinder also equipped with a dip tube. Fluorination was continued for a day at 95°C at a similar flow rate. 22.2 g of pure product were isolated. The product was identified by its characteristic mass spectrum.

Example 3B.

$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OH + NaH \rightarrow$
$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2ONa$ (1)

$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2ONa + H_2C{=}CH(CF_2)_3CF_3 \rightarrow$
$F[CF(CF_3)CF_2O]_5CF(CF_3)CH_2OCH_2\text{-}CH{=}CF(CF_2)_2CF_3$ (2)

A perfluoropolyether alcohol (KRYTOX alcohol, available from E. I. du Pont de Nemours & Company, Wilmington, Delaware; 55.51 g) of average molecular weight of 1586 g/mole was poured into a 50- ml round-bottomed flask with tetrahydrofuran (25 ml) and agitated with magnetic stirring. Next, sodium hydride (2.00 g, 0.084 mole) was added slowly via an addition funnel to the same reaction flask. The contents were stirred until no more evolution of hydrogen gas was evident. 1H,1H,2H-Perfluorohexane, (ZONYL PFBE, perfluorobutylethylene, available from E. I. du Pont de Nemours and Company, Wilmington, Delaware; 35 ml, 0.207 mole) was then added in a 6-mole excess to the poly(hexafluoropropylene oxide) sodium alkoxide and refluxed at 59°C for 24 hr. According to ^{1}H-NMR the percent conversion to the n-hexyl intermediate was calculated to be 86 %. Yield of total oil = 44.89 g.

$F[CF(CF_3)CF_2O]_{nn}CF(CF_3)CH_2OCH_2\text{-}CH{=}CF(CF_2)_2CF_3 + F_2\ (20\%) / N_2\ (80\%)$
$\rightarrow F[CF(CF_3)\text{-}CF_2\text{-}O\text{-}]_{(nn+1)}(CF_2)_5\,CF_3$ where nn is a number of 5 to 15.

The product of the above procedure were combined in an FEP tube reactor (O.D. 5/8 ") equipped with an FEP dip-tube and treated with 20% F2 / 80% N2 at ambient temperature at a rate of ca. 30 ml/min for 2 days at which time the contents were transferred to a 300 ml stainless steel cylinder also equipped with a

dip tube. Fluorination was continued for a day at 95 °C at a similar flow rate. The product was identified by its characteristic mass spectrum.

TEST METHOD AND RESULTS

Test Method. Procedure for Measuring Thermal Stability

A 75-ml stainless steel HOKE cylinder topped with a 10-cm stainless steel spacer and valve was used to contain the poly(HFPO) sample for each thermal stressing experiment. The mass of the cylinder was taken and recorded after every step in the procedure. In a dry box, the cylinder was charged with AlF_3 (ca. 0.05 g), weighed, and then charged with about 1 g sample of monodisperse poly(HFPO) containing different end groups. (The AlF_3 used in these experiments was synthesized by the direct fluorination of $AlCl_3$ and was shown by X-ray powder diffraction to largely be amorphous.) The cylinder was then removed from the dry box and placed in a thermostatic oil bath at a predetermined temperature in the range of 200-270 ± 1.0 °C. The valve was kept cool by diverting a stream of room-temperature compressed air over it. After a period of 24 hours, the cylinder was cooled to room temperature, weighed, and then cooled further to liquid nitrogen temperature (-196 °C). Any non-condensable materials were stripped from the cylinder under dynamic vacuum. The cylinder was then warmed to room temperature, and the volatile materials were removed by vacuum transfer and stored for later analysis by FT-IR and NMR spectroscopy. Methanol was then added to the cylinder to convert any acid fluorides that might have resulted from the degradation to their corresponding methyl esters. The resulting non-volatile material was then separated from any unreacted methanol and analyzed by GC-mass spectrometry. The results from this experiment as well as those from additional and related experiments where the monodisperse poly(HFPO) samples have either perfluoroisopropyl, perfluoroethyl, perfluoro-n-propyl, or perfluoro-n-hexyl end-groups are shown in Table 1.

Table 1

Temperature (°C)	200	210	220	230	240	250	260	270
Percent of $F[HFPO]_6$-CF_2CF_3 (Comparative Example A) degraded	--[a]	37.4[c]	96.3[c]	--	--	--	--	--
Percent of $F[HFPO]_7$-CF_2CF_3 (Comparative Example B) degraded	1.8	30.8	--	--	--	--	--	--
Percent of $F[HFPO]_6$-$CF(CF_3)_2$ (Example 1) degraded	--	6.2	14.2[b], 13.6	12.6	11.7	76.8	51.9	86.2
Percent of $F[HFPO]_7$-$CF_2CF_2CF_3$ (Example 2) degraded	--	--	86.5	--	--	--	81.8	--
Percent of $F[HFPO]_6$-$(CF_2)_5(CF_3)$ (Example 3) degraded	--	--	59.4	--	--	100	--	--

[a] --, not determined. [b] Replicates, [c] Average of triplicates.

Table 1 shows a substantial reduction in the amount of degradation of a poly(HFPO) fluid having a normal perfluoropropyl group on one end and any group C_3 to C_6 on the other as compared with the poly(HFPO) containing a normal perfluoropropyl end group on one end and perfluoroethyl end group on the other, demonstrating the greater stabilizing effect of the perfluoro C_3 to C_6 terminal groups.

Example 4. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2I$ from the corresponding secondary iodide $CF_3(CF_2)_2(OCF(CF_3)CF_2)_nOCF(CF_3)I$ having n''~8.

The polyhexafluoropropylene oxide homopolymer (HFPO) secondary iodide, $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{n''}OCF(CF_3)I$ having n~8, used as the starting material in this example, was made by first adding lithium iodide (Aldrich Chemical, Milwaukee, WI) (117.78 g) to a nitrogen-purged 2-L PYREX round-bottomed flask. KRYTOX Acid Fluoride (907.18 g) (available from E.I. du Pont de Nemours Co., Inc, Wilmington, DE) was then added to the flask, and the mixture was heated at 180 °C for 15 hours with stirring. The oil was filtered through a CELITE bed and analyzed by mass spectrometry and ^{13}C NMR spectroscopy. From the mass spectrum, fragments at 227 m/z ($-CFICF_3$) and 393 m/z ($-CF(CF_3)CF_2OCFICF_3$) are indicative of the secondary iodide. Nuclear magnetic resonance (NMR) analysis showed the carbon bonded to iodine at 78.1

ppm d,q; $-CFICF_3$; $^1J_{CFI} = 314.8$ Hz, $^2J_{CF3} = 43.3$Hz (^{13}C NMR: 75.5 MHz, D_2O/TMS).

Polyhexafluoropropylene oxide homopolymer (HFPO) secondary iodide (200.0 g, prepared as above) was added to a 500-mL PYREX round-bottomed flask and heated to 220 °C for 4 hours with stirring. The oil was filtered through CELITE (a SiO_2 filter aid), and analyzed by mass spectrometry and ^{13}C NMR spectroscopy. The HFPO primary iodide was identified by mass spectrometry analysis, mass fragments of m/z = 277 ($-CF(CF_3)CF_2I$) and m/z = 177 ($-CF_2I$) prove the structure of the desired product. By ^{13}C NMR spectroscopy, peaks specific to the desired product were detected at 93.8 ppm (t,d, $-CF(CF_3)CF_2I$, $^1J_{CF}$ = 332.94 Hz, $^2J_{CF}$ = 33.19 Hz) and at 93.9 ppm (t,d, $-CF(CF_3)CF_2I$, $^1J_{CF}$ = 332.94 Hz, $^2J_{CF}$ = 33.19 Hz). Yield: 187.0 g.

Example 5. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2I$ from KRYTOX Acid Fluoride having n~8.

Lithium iodide (187.71 g) was added to a nitrogen purged 2-L PYREX round-bottomed flask. Upon addition of KRYTOX Acid Fluoride (1,651.3 g), the flask was heated at 220 °C for 15 hours with stirring. The oil was filtered through CELITE and determined to be identical to the above product. Yield 1447.6 g.

Example 6. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2I$ from KRYTOX Acid Fluoride having n~8.

Calcium iodide (Aldrich Chemical, Milwaukee, WI) (20.72 g) was added to a nitrogen purged 500-ml round-bottomed flask in a dry box. Next, KRYTOX Acid Fluoride (100.00 g) was added, and the mixture was heated at 220 °C for 12 hours with stirring. The product was allowed to cool to room temperature and was filtered through CELITE. The product was consistent with earlier results. Yield 60.62 g.

Example 7. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2I$ from KRYTOX Acid Fluoride having n~6.

Barium iodide (Aldrich Chemical, Milwaukee, WI) (5.00 g) was added to a nitrogen purged 50-mL round-bottomed flask. Next, KRYTOX Acid Fluoride (13.1 g) was added to the flask. The reaction mixture was heated at 220°C for 12

hours while stirring. The primary iodide was identified by GC/MS and was consistent with earlier results. Yield: 5.1 g.

Example 8. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2I$ from KRYTOX Acid Fluoride having n~52.

Lithium iodide (52.0 g) was added to a nitrogen purged 5-L PYREX round-bottomed flask. Upon addition of KRYTOX Acid Fluoride (2720 g), the mixture was heated at 220 °C for 20 hours with stirring. The oil was filtered through CELITE and determined to be the desired products. Yield 2231.76 g.

Example 9. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{(n''-1)}OCF(CF_3)CF_2Br$ from the corresponding acid fluoride.

Step 1. 5.57 g $F(CF(CF_3)CF_2O)_5CF(CF_3)COF$, 0.53 g $AlBr_3$ (Aldrich Chemical, Milwaukee, WI), and 2.65 g BBr_3 (Aldrich Chemical, Milwaukee, WI) were loaded into a 75-ml stainless steel cylinder in a glove box. The cylinder was closed with a valve and kept at ambient temperature for 24 h with occasional shaking. After that, the liquid content was removed with a pipette and filtered. The subsequent ^{13}C NMR spectroscopy shows quantitative conversion of the Acid Fluoride to the acid bromide.

Step 2: Conversion of the acid bromide to the HFPO primary bromide. 3.82 g of product from above was loaded into a 75-ml stainless steel cylinder within a glove box, closed with a valve, evacuated, weighed, and heated to 250 °C for 16 h. Additional heating to 340 °C overnight produced 0.08 g CO and other volatiles. Investigation of the liquid residue by ^{13}C NMR spectroscopy showed total disappearance of the acid bromide and new signals for the primary bromide. Along with the other signals expected, the chemical shift for the $-CF_2Br$ carbon is found at $\delta = 115.6$ ppm; t, d; $^1J_{CF2} = 313.8$ Hz, $^2J_{CF} = 32.5$ Hz thus establishing the identity of the desired product.

Example 10. Preparation of $CF_3(CF_2)_2(OCF(CF_3)CF_2)_{n''}OCF(CF_3)CF_2Br$ from the corresponding Iodide.

Poly(hexafluoropropylene oxide) primary iodide (469.3 g) prepared, as in Example 6, was added to a nitrogen purged 500-ml round-bottomed flask. With stirring, carbon tetrabromide (Aldrich Chemical, Milwaukee, WI) (115.9 g) was

charged to the flask and heated slowly to 175-185 °C and held at that temperature for 3 days. The primary bromide was identified by mass spectrometry, with mass fragments of m/z = 229 and m/z = 231 (-CF(CF_3)CF_2Br) and m/z = 129 and m/z = 131 (-CF_2Br) being indicative of the HFPO primary bromide. Yield: 299 g.

Comparative Example C

(Method A) A thermal reaction was attempted between KRYTOX Acid Fluoride and sodium iodide (Aldrich Chemical, Milwaukee, WI) at a temperature of 220 °C. Sodium iodide (27.11 g) and KRYTOX Acid Fluoride (186.34 g) were added to a nitrogen purged 500-ml round-bottomed flask equipped a thermocouple and reflux condenser. The reactants were heated at 220°C for 12 hours while stirring. The product was filtered through CELITE and analyzed with mass spectrometry. No reaction was observed.

(Method B) A reaction was attempted between KRYTOX Acid Fluoride, sodium iodide, and acetonitrile at 50 °C to reproduce prior art as reported in US Patent 5,278,340. Sodium iodide (42.85 g) and KRYTOX Acid Fluoride (160.00 g) were added to a nitrogen purged 250-ml round-bottomed flask equipped with a thermocouple and reflux condenser. Next, acetonitrile (7.00 g) was added. The reactants were stirred while heating at 50 °C for 12 hours. The product was filtered through CELITE and analyzed by mass spectrometry. No reaction was observed.

Comparative Example C demonstrates that sodium iodide alone or sodium iodide dissolved in acetonitrile does not form a poly(hexafluoropropylene oxide) iodide.

Comparative Example D

Potassium iodide (Aldrich Chemical, Milwaukee, WI) (36.52 g) was added to a nitrogen purged 500-ml round-bottomed flask and heated at 110 °C for 30 min to dry the salt. Next, KRYTOX Acid Fluoride (226.79 g) was added to the flask and the contents of the flask were heated at 180°C for 12 hours. After the reaction, the product was filtered through CELITE and analyzed by mass spectrometry. No reaction was observed.

Comparative Example D demonstrates that potassium iodide cannot be used to form a poly(hexafluoropropylene oxide) iodide.

Comparative Example E

Lithium bromide (Aldrich Chemical, Milwaukee, WI) (25.0 g) was added to a nitrogen purged 50-ml round-bottomed flask. Next, KRYTOX Acid Fluoride (149.0 g) was added to the reaction flask. The reaction mixture was heated at 220°C for 12 hours with stirring. The product was washed with methanol, then water, and analyzed by mass spectrometry. No reaction was observed.

Comparative Example E demonstrates that lithium bromide cannot be used to form a poly(hexafluoropropylene oxide) bromide.

CLAIMS

1. A composition comprising a perfluoropolyether, which comprises perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and 1,2-bis(perfluoromethyl)ethylene diradical, $-CF(CF_3)CF(CF_3)-$, is absent in the molecule of said perfluoropolyether.

2. A composition according to claim 1 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.

3. A composition according to claim 1 or 2 wherein said perfluoropolyether has the formula of $C_rF_{(2r+1)}$-A-$C_rF_{(2r+1)}$; each r is independently 3 to 6; if r = 3, both end groups $C_rF_{(2r+1)}$ must be a propyl radical; A is selected from the group consisting of $O-(CF(CF_3)CF_2-O)_w$, $O-(C_2F_4-O)_w$, $O-(C_2F_4-O)_x(C_3F_6-O)_y$, $O-(CF_2CF_2CF_2-O)_w$, $O-(CF(CF_3)CF_2-O)_x(CF_2CF_2-O)_y-(CF_2-O)_z$, and combinations of two or more thereof; w is 4 to 100; and x, y, and z are each independently 1 to 100.

4. A composition comprising a perfluoropolyether, which has the formula selected from the group consisting of $F(C_3F_6O)_zCF(CF_3)CF_2X$, $XCF_2CF(CF_3)O(C_3F_6O)_pR_f^2O(C_3F_6O)_nCF(CF_3)CF_2X$, $XCF_2CF_2O(C_3F_6O)_xCF(CF_3)CF_2X$, $(R_f^1)(R_f^1)CFO(C_3F_6O)_xCF(CF_3)CF_2X$, and combinations of two or more thereof wherein X is I or Br, x is a number from 2 to about 100, z is a number from about 5 to about 100, p is a number from 2 to about 50, n is a number from 2 to about 50, a is 1 or 2, each R_f^1 is independently a monovalent C_1 to C_{20} branched or linear fluoroalkane, and R_f^2 is a divalent C_1 to C_{20} branched or linear fluoroalkane.

5. A composition according to claim 1, 2, 3, or 4 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

6. A composition according to claim 5 wherein said thickener is selected from the group consisting of poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof.

7. A process for producing a perfluoropolyether comprising (1) contacting a reactant with a metal halide to produce an alkoxide wherein said reactant is a perfluoro acid halide, a C_2 to C_4-substituted ethyl epoxide, a C_{3+} fluoroketone, or combinations or two or more thereof; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to its corresponding alcohol; (5) converting said corresponding alcohol with a base to a salt; (6) contacting said salt with a C_{3+} olefin; and (7) fluorinating said fluoropolyether.

8. A process according to claim 7 wherein said C_{3+} olefin is a C_3-C_6 straight chain olefin, C_3-C_6 branched chain olefin, C_3-C_6 allyl halide, or combinations of two or more thereof.

9. A process according to claim 8 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

10. A process according to claim 8 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce an acid halide; (3) contacting said acid halide with a metal iodide to produce a second iodide; (4) fluorinating said second iodide.

11. A process according to claim 8 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) contacting said second acid halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; and (5) fluorinating said third iodide.

12. A process according to claim 11 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting

said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second halide; (3) contacting said second halide with a metal iodide to produce a second iodide; (4) contacting said second iodide with an olefin to produce a third iodide; (5) dehydrohalogenating said third iodide to give a second olefin; and (6) fluorinating said second olefin.

13. A process according to claim 8 wherein said process comprises fluorinating a fluoropolyether having alkyl radical end groups; said radical has at least 3 carbon atoms per radical and is substantially free of methyl and ethyl; and a 1,2-bis(methyl)ethylene diradical, $-CH(CH_3)CH(CH_3)-$, is absent in the molecule of said fluoropolyether, optionally said process is carried out in the presence of a mixture comprising an inert solvent and a hydrogen fluoride scavenger.

14. A process according to claim 8 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second halide; (3) contacting said second halide with a metal iodide to produce a second iodide; (4) replacing the iodine radicals of said second iodide with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and (5) fluorinating said fluoropolyether.

15. A process according to claim 8 wherein said process comprises (1) contacting said reactant with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second halide; (3) esterifying said second halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with sulfur tetrafluoride or derivative thereof to convert the OH groups of said alcohol to fluorine radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

16. A process according to claim 8 wherein said process comprises (1) contacting a fluorotertiary alkoxy-containing compound with a first fluoropolyether to produce a second fluoropolyether and optionally (2) fluorinating said second fluoropolyether wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol or a perfluoro-t-butyl

hypofluorite; said first fluoropolyether has (i) a starting C_3-C_6 segment or $R_f^8(R_f^9)CFO$ segment and (ii) a -A-O-C(CF_3)=CF_2 or a -A-O-C(CF_3)=CHF intermediate end group; R_f^8 is $C_jF_{(2j+1)}$; R_f^9 is $C_kF_{(2k+1)}$; j and k are each ≥ 1; (j + k) ≤ 5; and A is selected from the group consisting of O-($CF(CF_3)CF_2$-O)$_w$, O-(CF_2-O)$_x$(CF_2CF_2-O)$_y$, O-(C_2F_4-O)$_x$, O-(C_2F_4-O)$_x$(C_3F_6-O)$_y$, O-($CF(CF_3)CF_2$-O)$_x$(CF_2-O)$_y$, O($CF_2CF_2CF_2O$)$_w$, O-($CF(CF_3)CF_2$-O)$_x$(CF_2CF_2-O)$_y$-(CF_2-O)$_z$, and combinations of two or more thereof.

17. A process according to claim 16 wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol a perfluoro-t-butyl hypofluorite.

18. A composition comprising a perfluoropolyether, which has the formula of $F[C_3F_6O]_{z'}CF(CF_3)CF_2X$, $F[C_3F_6O]_{x'}CF_2CF_2X$, $XCF_2CF(CF_3)O(C_3F_6O)_{p'}R_f^{2'}O(C_3F_6O)_{n'}CF(CF_3)CF_2X$, $XCF_2CF_2O(C_3F_6O)_{x'}CF(CF_3)CF_2X$, $(R_f^{1'})(R_f^{1'})CFO(C_3F_6O)_{x'}CF(CF_3)CF_2X$, or combinations of two or more thereof wherein X is I or Br, x is a number from 2 to about 100, z' is a number from about 5 to about 100, p' is a number from 2 to about 50, n' is a number from 2 to about 50', each $R_f^{1'}$ is independently a monovalent C_1 to C_{20} branched or linear fluoroalkane, and $R_f^{2'}$ is a divalent C_1 to C_{20} branched or linear fluoroalkane.

19. A composition according to claim 1 wherein said composition is said perfluoropolyether.

20. A process comprising contacting (1) a perfluoropolyether acid fluoride with a metal bromide or metal iodide or (2) heating a perfluoropolyether secondary halide, under a condition sufficient to effect the production of a perfluoropolyether comprising at least one bromine or iodine in the primary position of one or more end groups of the perfluoropolyether wherein said process is carried out substantially free of a solvent and said acid fluoride moiety comprises -$CF_2OCF(CF_3)COF$ moiety.

21. A process according to claim 20 wherein process comprises contacting said perfluoropolyether primary iodide with carbon tetrabromide.

22. A process according to claim 20 wherein said process comprises contacting said perfluoropolyether acid fluoride with mixed metal bromides, mixed metal iodides, or combinations thereof.

23. A process according to claim 22 wherein said mixed metal bromide and iodide is a mixture of aluminum bromide and boron bromide.

24. A process according to claim 20 wherein the metal moiety of said metal bromide or metal iodide is selected from the group consisting of lithium, calcium, barium, aluminum, boron, and combinations of two or more thereof.

25. A process according to any one of claims 20-24 wherein said perfluoropolyether acid fluoride comprises repeat units derived from the group consisting of $-CF_2O-$, $-CF_2CF_2O-$, $-CF_2CF(CF_3)O-$, $-CF(CF_3)O-$, $-CF(CF_3)CF_2O-$, $-CF_2CF_2CF_2O-$, $-CF(CF_s)O-$, $-CF_2CF(CF_s)O-$, $-CF_2CF(CF_2CF_3)O-$, $-CF_2CF(CF_2CF_2CF_3)O-$, $-CF(CF_2CF_3)O-$, $-CF(CF_2CF_2CF_3)O-$, $-CH_2CF_2CF_2O-$, $-CF(Cl)CF_2CF_2O-$, $-CF(H)CF_2CF_2O-$, $CCl_2CF_2CF_2O-$, $-CH(Cl)CF_2CF_2O-$, and combinations of two or more thereof.

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WO 02/006375 A3

(54) Title: PERFLUOROPOLYETHERS AND PROCESSES THEREFOR AND THEREWITH

(57) Abstract: A perfluoropolyether, a composition comprising the perfluoropolyether, a process for producing the perfluoropolyether, and a process for improving the thermostability of grease or lubricant are provided. The perfluoropolyether comprises (1) perfluoroalkyl radical end groups in which the radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl end groups or (2) at least one bromine or iodine atom at the primary position of the perfluoropolyether.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/22817

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G65/00 C08G65/22 C10M107/38 C08G65/323

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 90 03353 A (EXFLUOR RES CORP) 5 April 1990 (1990-04-05) cited in the application examples 31,33	1,2,5-8, 13,19
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X	EP 0 381 086 A (HOECHST AG) 8 August 1990 (1990-08-08) claim 5 example 6	1,2

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
31 May 2002	21.06.02

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	O'Sullivan, T

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 174 461 A (ZAMBONI VALENTINO ET AL) 13 November 1979 (1979-11-13) claim 1 example 1 column 8, line 45 - line 65	1-3, 5-13,19
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [X] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[X] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-3,5(part),6(part),7-17,19

   Perfluoropolyethers containing fluoroalkyl end-groups with more than 3 carbon atoms and methods for preparing them.

2. Claims: 4,5(part),6(part),18,20-25

   Perfluoropolyethers terminated with either iodine or bromine atoms.

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